IJBST

ISSN: 0974 – 3987
IJBST (2016), 9(5):27-33

Distribution of trace metals in water, sediments and algal mats of Bodo creek on River Niger Delta, Nigeria

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Abstract

The distribution of trace metals (Fe, Mn, Ni, Cd, Cr, Co, Cu, Pb, and Zn) in surface water, sediments and algal mat collected from four locations on Bodo Creek were assessed using inductively coupled plasma mass spectrometer (ICP MS). The physicochemical parameters (temperature, pH, DO, BOD and COD) of water; pH, particle size and organic matter of sediments and algal mat were analyzed. The mean values of BOD and COD exceeded the accepted maximum permissible levels for domestic use in Nigeria. Except for Cu and Zn that were highest in water, the trace element concentrations in these environmental matrices were generally in the following order: Algae > sediments> water. Apart from Cd that was below detective limit, the trace metal contents in water were higher in concentration when compared with international standards for public surface water. Positive significant correlation existed between Mn and Fe and with other metals except Cd in all the matrices. This implies that these metals often sorbed to iron and manganese complexes. Metals accumulated more in algae and could be integrated in remedial actions to consider in environmental management of water pollution in River Niger delta.

Keywords: Algal mat, oil spill, Bodo creek, surface water and sediments

INTRODUCTION

Bodo water system is a network of tidal brackish creeks flanking Bodo Community on the upper reach of the Andoni–Bonny River in Niger delta. Bodo creek is prone to crude oil spills and the magnitude of oil released into this system has not been quantified correctly [1]. The consequences of oil exposure to aquatic ecosystem include impacts on the health of organisms, introduction of toxic pollutants into the different matrices of the aquatic ecosystem as well as changes in complex interrelations between biota and their physical environment. Any harm to the physical environment will often affect one or more species in a food chain, which may affect other species further up or down the chain.

Trace metal contamination is one of the important pollutants in the aquatic ecosystem. Studies have linked high concentrations of some metals in the Niger Delta with continuous oil spill in the region [2, 3]. Metals are non-biodegradable and persist for a long time in the environment. They tend to be trapped in the aquatic environment and accumulate in sediments which may act as sinks and source of further contamination in aquatic systems. The accumulation of trace metals in sediment is controlled by the size of sediment particles which affect their capacity to take in these metals [4, 5]. Under favorable physic-chemical conditions in the sediment, metals can remobilize and release to the water column [6]. However, the relationship on the distribution of metals in sediments, water and algal mat is not well known in Niger delta. Sequestration of metals by algae has been studied by different researchers [7, 8]. Their studies have shown that differential accumulation of metals do occur under favorable physicochemical properties of water and sediment [9]. Algae in a particular water body could be used for removal or bio-monitoring of metal pollution because there is a relationship between the amount of metal accumulated by algae and the concentration of the same metal in water [10, 11]. They stated that the concentration factor for heavy metals varies greatly in different algal species but it increases as the metal concentration in water decreases.

Oil pollution in Niger delta is a major environmental concern internationally. The recent UNEP report on Ogoni land has necessitated a cleanup of the region including Bodo creek [12]. The use of natural alternative could be considered as an option in this

cleanup to reduce environmental impact of the action, and it is cost- effective. Conspicuous dark green algal mats are abundant on the surface of the sediment in this area and there is need to consider their relationship with water and sediment which can be leverage on during the cleanup activities.

The objective of this study is to evaluate the concentrations of trace metals, Cu, Zn, Co, Ni, Mn, Fe, Cd, Hg and Cr in algal mat, sediment and water from Bodo creek in Niger Delta wetland. The distribution of trace metals in these compartments of the aquatic environment will indicate the health status of the wetland systems and provide insight on the biodegradation role of algae which is important for environmental management programs in the region.

MATERIALS AND METHODS

Study area

Four locations with history of oil pollution or are close to oil production facilities were selected on Bodo Creek as shown in Figure 1. Station 1 is situated upstream ($7^0$16.074″E; $4^0$37.240″N), close to oil pipeline in a forested mangrove area and the water is for domestic use. Station 2 is located on a vast de-vegetated tidal flat coated with oil. The edge of the supralittoral shores is lined with unproductive coconut trees ($7^0$16.071″E; $4^0$36.263″N).

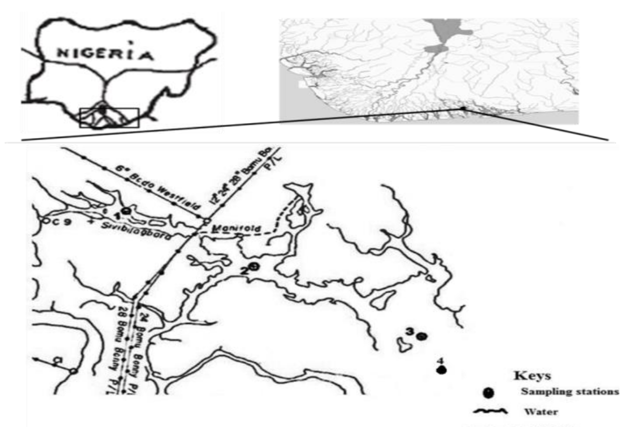

Figure 1. Map of study site

Station 3 is situated $7^0$16.804″E; $4^0$36.259″N, the vegetation is dominantly by roots of black mangrove with no stems and are completely coated in oil. Station 4 is located downstream ($7^0$16.998″E; $4^0$36.342″N) and the vegetation similar to station 3 and is closed to abandon bridge construction.

Sample collections

At each location, four sub-samples of algal mat and sediment respectively were collected from randomly selected nodes using plastic trowel. Care was taken not to disturb the fine surface algae flock which was collected first and the sediments were collected at depths ranging from two to thirty centimeters. The samples were homogenized to form a representative sample. Water samples were collected against the flow of the water using pre-cleaned 500ml polyethylene bottles. A total of 48 samples were collected during the wet season (May 2013). The composite samples were preserved in separate sampling packs, sealed and taken to the laboratory in a cool box. All samples were stored at 5°C prior for further analysis.

Physiochemical Analysis

Standard methods were used to determine the physico-chemical parameters (temperature, pH, Dissolved Oxygen (DO), Biological Oxygen Demand (BOD), and Chemical Oxygen Demand (COD)) of surface water [13].

Particle size analysis was carried out on sediment and algal mat using a laser granularmeter (Coulter LS 230 with P.I.D.S.) after filtering with 2 µm sieve. Weight loss-on-ignition (LOI) in a preheated muffle furnace at 450 °C for 4 h was used to calculate organic matter in sediment and algal mat [14]. The pH was measured in a suspension of 25 ml de-ionized water to 10 g of sediment after shaking for 2 h using a pH meter (model HI 2211, Hanna).

Metal analysis

To determine the metals in water, 2 mLs of concentrated (90 %) nitric acid was added to 0.2 mLs of water sample and made up to 10 mLs with deionized water (x 5 dilution). This was analyzed using inductively coupled plasma mass spectrometer (ICP MS: model X7, Thermo Electron).

Sediment samples were air dried; aliquots of 0.25 g and 2 mLs of concentrated (90 %) nitric acid were weighed into a Teflon inset of microwave digestion vessel. The same process was repeated for algal mat.

Metals were extracted from algae and sediment using Microwave Accelerated Reaction System (MARS Xpress) at 1500 W powers (100 %), ramped to 175 °C in 5.5 min, and held for 4.5 min. The digests were allowed to cool-down for 1 h and subsequently filtered through Whatman 42 filter paper. It was then transferred quantitatively to a 100 mL volumetric flask by adding deionized water. Metal concentrations were analyzed using ICP-MS and the concentrations expressed in mg/kg.

All chemicals and reagents used were of analytical grade. One analytical blank solution was prepared in the same way as the samples for every set of 12 samples. Certified reference materials (CRM 049-050) were used to confirm the procedures used.
Statistical analyses were performed using Minitab version 16 package and Microsoft Excel. Difference in the different aquatic systems were evaluated using Analysis of variance (ANOVA) and all statistical significance level was considered for $p<0.05$. Pearson’s Product Correlation was used to examine the relationship among the parameters analyzed.

RESULTS AND DISCUSSION

Physico-chemical parameters of water and sediments

In order to reduce metal pollution in marine environment, it is necessary to determine the mechanisms influencing their distribution, thus Water and sediment chemistry is commonly considered for assessment of metal pollution in aquatic environment. The Mean values of studied physicochemical parameters are presented in Table 1.

Temperature, DO and pH had the lowest values at stations 1, while BOD and COD decreased from station 1 to station 4. The mean temperature ranges from 27.4 – 31.9 ºC; DO ranges from 5.3 to 6.3 Mg/L and pH ranges from 6.1 to 7.5. The mean values of BOD and COD exceeded the Department of Petroleum Resources accepted maximum permissible levels for domestic use in Nigeria [15].

The sediment was acidic with minimum pH of 4.7 recorded in stations 1 and 4; pH of 5 in station 2; and the maximum pH of 6.0 recorded in station 3. The relative particle size in Bodo creek is presented in Figure 2. Their abundance was in following order: sand > silt > organic matter > clay. In general, samples were dominated by sand which ranges from 65 to 77 % in sediment and 54.9 to 68 % in algal mat. Higher percent of sand were found in sediment than in algal mat for all the stations. Higher concentration of sandy sediments at Bodo creek is due to tidal effects which play major roles in the deposition of sand there. However, the silt values were higher in algal mat than in sediments for all the stations. Silt contents in sediment ranged from 10.2 % in station 1 to 32.5 % in station 3 while silt contents in algal mat ranged from 29.9 % in station 2 to 41.6 % in station 1. Similarly, the organic matter in algal mat (16-39 %) was higher than that of sediment (2.7 – 9.4 %). Clay contents were low; the highest values were in station 1 for sediment (2.6 %) and algal mat (2.1 %) respectively. The sediments of Bodo creek are very sandy in nature with very low organic matter [16]. Contrary to this, higher values of organic matter were recorded in algal mats.

Distribution of metals in water, sediment and algal mat from Bodo creek

Trace metals analyzed in this study were in form of 56Mn, 56Fe, 59Co, 60Ni, 65Cu, 66Zn, 111Cd, 208Pb, 835Cr. Except for Cu and Zn that had the highest values in water, the trace element concentrations in these environmental matrices were generally in the following order: Algae > sediments > water. Table 2 presents the mean ± Standard Deviation (SD) of concentrations of trace metal in the surface water of all stations studied in Bodo creek. The order of abundance of elements in sediment is Fe > Mn > Zn > Cu > Cr >Pb = Ni > Co > Cd, which is in agreement with finding of [17]. The average metal values (Mg/kg) in water were 44 in Mn, 366 in Fe, 0.4 in Co, 1.5 in Ni, 27 in Cu, 107 in Zn, -0.9 in Cd, 1.5 in Pb and 2.9 in Cr. Lead (Pb), Cr, Cu, Ni were highest while Mn, Co were lowest in station 1. Dissolution of Fe and Mn is facilitated at low dissolved oxygen and pH which can be converted to complex hydroxy compounds that may precipitate with time. The concentrations of the metals in Bodo water were higher than WHO [18] established guideline values except for Mn, Fe, and Zn which they stated were not of health concern at levels causing acceptability problems or found in drinking-water.

The mean concentrations ± Standard Deviation (SD) of metals in sediment from Bodo creek is presented in Table 3. The abundance of elements in sediment is in order of Fe > Mn > Zn > Cr > Cu > Pb > Ni > Co > Cd. Except for cadmium and Zn, the study results indicated that station 4 had the highest concentration for the other metals. The mean values (Mg/kg) of the metals were 45 (Mn), 6101 (Fe), 1.48 (Co), 2.06 (Ni), 0.02 (Cd), 7.7 (Cu), 17.1 (Zn), 2.9 (Pb), and 16.7 (Cr). The metal contents appeared lower than reported natural abundance of the metal in the crustal rocks using the world shale value [19]. Fe and Mn are ubiquitous in sediment and their occurrence is primarily controlled by pH and dissolved oxygen [20]. Metals are generally more concentrated in the fine granulometric fractions than in the coarse ones [5]. The stations that contain the greatest concentration of metals had higher organic matter and lesser sand.

In algae, the metal (Mg/kg) ranges were Mn (11-86.5), Fe (7337.13-17452), Co (0.5-5.7), Ni (2.2-9.4), Cu (7.8-30.39), Zn (27-34), Pb (0.15-7.5), Cr (25-45). The mean values of metal in algae were 48 (Mn), 13579 (Fe), 4 (Co), 7 (Ni), 24 (Cu), 31 (Zn), -0.03 (Cd), 7.2 (Pb), and 36 (Cr). Which has a similar abundance order of Fe > Mn > Cr > Zn >Cu > Pb > Ni > Co > Cd. Except for cadmium, Pb and Zn, station 1 had the highest concentration for the other metals. From the study, higher concentrations of metals were either in station 1 or station 4 which has the lowest pH value. Earlier works has suggested that majority of the metal binding groups of algae are acidic and their availability is pH-dependent. These groups create a negatively charged surface at acidic pH, and electrostatic interactions between cationic species and the cell surface is responsible for metal bio-sorption [7]. Influence of pH on metal sorption can also be related to the concentration and availability of free metal ions in water. Availability of metal ions for binding onto algae depends on chemical speciation.

Iron content being higher than all the metals was observed in Niger delta in agreement with other works [16].

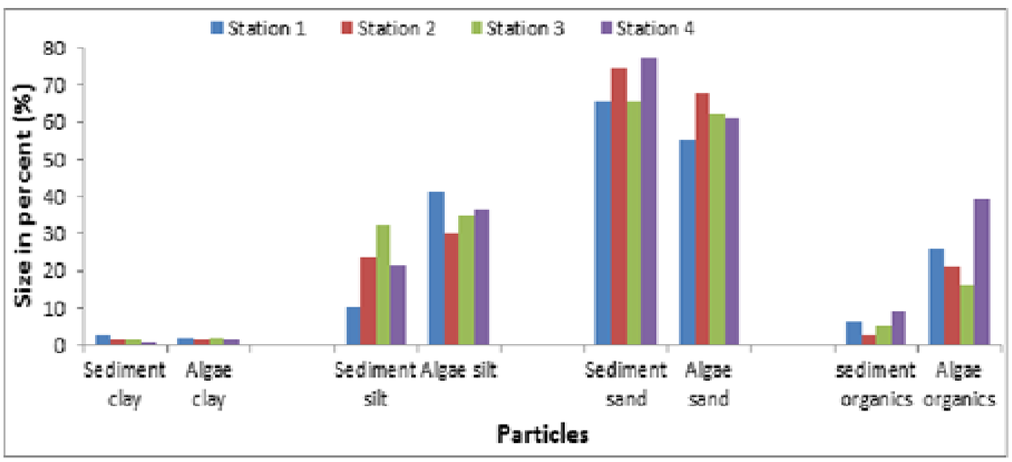

Figure 2. Particle size and organic matter in different stations of Bodo creek

Table 1. Variations in physico-chemical parameters of Bodo Creek in comparison with national standards in Nigeria.

Parameters	**Stations**				**Coefficient of Variance**	
	1	**2**	**3**	**4**	**CV**	**DPR(2002)**
Temp(^{O}C)	27.4±0.1a (27.3-27.5)	31.9 ± 0.2b (31.7-32.0)	30.03± 0.01c (30.02-30.04)	30.20± 0.26c (30.0-30.5)	0.04-0.87	30
pH	6.1±0.02a (6.10-6.12)	7.5±0.1b (7.4-7.6)	7.4±0b (7.40-7.45)	7.4 ±0.2b (7.20-7.51)	0.3-2.2	6-9
DO(Mg/L)	5.3±0.3a (5.3-5.6)	6.0±0.1b (5.1-6.1)	6.3±0.20b (6.11-6.50)	6.2±0.06b (6.12-6.23)	0.89-5.71	20
BOD(Mg/L)	33.3±3.1a (30.0-36.0)	28.3±0.6a (28.0-29.0	22±2b (20-24)	22.00±1.73 b (21.00-24.00)	2.04-9.17	10
COD(Mg/L)	84.3±2.6a (82.1-87.2)	83.4±2.2a (81.3-5.6)	55.8 ±1.8b (54.0-57.6)	53.3 ±1.4b 52.1-54.8	2.58-3.20	30

Notes: (n - 24). Values are mean ± SD and range values in parentheses. Values in each row with the same superscript are not significantly different at $p < 0.05$. DPR _ Department of Petroleum Resources (2002) limits for substances discharge into water for domestic use in Nigeria.

Table 2. Concentrations of metals (Mg /kg) in Water of Bodo Creek in comparison with international Standards.

Metals	Station1	Station 2	Station 3	Station 4	Mean	WHO 2011
Mn	34±2a	45±13.2a	41±12a	55.61±13a	44	-
Fe	403±19a	423±41a	469±5a	170.4±59a	366	-
Co	0.2±0.3a	0.5±0.2a	0.5±0.2a	0.39±0.08a	0.4	-
Ni	1.8±1.9a	1.5±1.4a	1.6±0.7a	1.31±0.34a	1.5	0.07
Cd	-0.5±0.1a	-0.9±0.2a	-1.0±0.1b	-0.09±0.04b	-0.89	0.003
Cu	36±2a	32±20a	23.7±23a	12.50±6.18a	27	2
Zn	123±6a	107±54a	135±57a,b	83.8±53.5a,b	107	-
Pb	3.8±1.1a	1.4±2.6a	0.8±1.9b	-0.11±0.41a	1.5	0.01
Cr	3.5±1.5a	2.9±1.1a	2.9±1.5a	2.37±1.345a	2.9	0.05

Notes: (n = 24). Values in each row with the same superscript are not significantly different at $p < 0.05$.

Table 3. Metal concentrations (Mg/kg) in sediment from Bodo Creek in comparison with shale values

Metals	Station 1	Station 2	Station 3	Station 4	Mean	shale values
Mn	27±15a	30±9.13a	10±2.21a	116±77.9b	45	850
Fe	7143±69a	4914±106a,b	2308±63b	10040±52a,c	6101	47200
Co	0.25±0.0a	1.4±0.3a	0.8±0.2a	3.41±1.7c	1.48	19
Ni	0.82±0.3a	2.2±0.61a	1.4±0.3a	3 .86±1.97c	2.06	68
Cd	0.03±0.1a	0.03±0.06a	-0.0±0.05a	-0.0±0.04a	0.02	0.3
Cu	7.61±1.2a	7.7±2.9a	5.8±3a,c	9.9±1.93a,c	7.7	45
Zn	38±21a	8.6±2.8b	5.8±3.4c,b	16±9 d,c	17.1	95
Pb	3.3±1.3a	2.4±0.71a	1.7±0.9a,b	4.47±2.21a,c	2.9	20
Cr	21±2a	13±2.9a,b	7.5±1.5b,c	26±12a,d	16.7	90

Values in each row with the same superscript are not significantly different at $p < 0.05$. Shale values from Turekian and Wedepohl (1961).

Table 4. Concentration (Mg/kg) of metals in Algae mat from Bodo Creek

Metals	Station 1	Station 2	Station 3	Station 4	Average
Mn	40.66±19a	86.5±79ab	11±3.8ac	54.5±33.80a	48
Fe	7337±82a	17452±127b	13709±198c	15817±191c	13578
Co	0.5±0.1a	5.7±0.5b	4.5±0.7c	5.3±0.56b,c	4
Ni	2.2±0.4a	9±0.9b	7.1±0.9c	9.4±0.4b,d	7
Cd	0.03±0.0a	-0.03±0.0a	-0.1±0.1b	-0.1±0.0b,c	0.03
Cu	7.8±2.5a	30±2.9b	28±5.31b	30±3.2b	24
Zn	34±19a	32±3.1a	27±2.85a	30±2.6a	31
Pb	4.1±0.9a	0.2±0.7b	7.1±1.37c	7.5±0.71c,d	7.6
Cr	25±2.1a	45±3.68ab	35.62±4.2b	40±4.4b	38

Notes: (n = 24). Values in each row with the same superscript are not significantly different at $p < 0.05$

Table 5. Pearson's correlation matrix

	S-pH	S-Mn	S-Fe	S-Co	S-Ni	S-Cu	S-Zn	S-Pb	S-Cr	Al-Fe	Al -Co	Al-Ni	Al-Cu	Al -Cd	Al-Pb	Al -Cr	temp	pH	DO	BOD	COD	AL-Org
S-pH	1																					
S-Mn	0.6	1																				
S-Fe	0.65	0.89	1																			
S-Co	0.52	0.96	0.82	1																		
S-Ni	0.51	0.94	0.8	0.98	1																	
S-Cu	0.53	0.65	0.71	0.59	0.6	1																
S-Zn	0.44	0.28	0.51	0.15	0.19	0.41	1															
S-Cd	-0	0.04	-0	0	0.04	0.49	0.07															
S-Pb	0.6	0.94	0.91	0.89	0.88	0.84	0.44	1														
S-Cr	0.67	0.85	0.99	0.76	0.74	0.71	0.54	0.88	1													
Al-Mn	-0.3	-0.09	0.02	0.02	0.1	-0.04	-0.08	-0.07	0.0													
Al-Fe	-0.2	0.38	0.06	0.56	0.6	0.05	-0.45	0.25	-0.03	1												
Al -Co	-0.2	0.37	0.01	0.55	0.57	0.04	-0.49	0.24	-0.08	0.98	1											
Al -Ni	-0.1	0.44	0.09	0.61	0.62	0.12	-0.46	0.31	-0.0	0.97	0.98	1										
Al-Cu	-0.1	0.34	-0-0	0.53	0.54	0.05	-0.51	0.22	-0.1	0.94	0.97	0.95	1									
Al-Zn	-0.1	0.19	0.15	0.28	0.26	0.23	-0.53	0.17	0.12	0.39	0.41	0.43	0.47									
Al -Cd	-0.1	-0.32	-0.1	-0.4	-0.4	-0.19	-0.06	-0.30	-0.0	-0.61	-0.6	-0.58	-0.65	1								
Al- Pb	-0.4	0.15	-0.1	0.35	0.39	-0.11	-0.6	0.03	-0.22	0.91	0.91	0.88	0.85	-0.33	1							
Al -Cr	-0.2	0.35	0.07	0.54	0.58	0.04	-0.4	0.24	-0.02	0.98	0.95	0.94	0.89	-0.5	0.92	1						
temp	-0.4	0.13	-0.2	0.32	0.36	-0.07	-0.54	0.03	-0.27	0.92	0.93	0.91	0.86	-0.44	0.94	0.92	1					
pH	-0.1	0.29	-0.1	0.48	0.51	-0.05	-0.53	0.14	-0.17	0.94	0.97	0.94	0.96	-0.58	0.89	0.90	0.91	1				
DO	-0.1	0.26	-0.1	0.43	0.44	-0.03	-0.51	0.12	-0.17	0.82	0.85	0.82	0.94	-0.68	0.68	0.73	0.70	0.88	1			
BOD	-0.1	-0.4	-0	-0.5	-0.5	0.08	0.43	-0.21	0.0	-0.66	-0.7	-0.71	-0.76	0.55	-0.51	-0.57	-0.50	-0.75	-0.81	1		
COD	-0.4	-0.47	-0.2	-0.5	-0.5	-0.08	0.18	-0.33	-0.10	-0.36	-0.4	-0.44	-0.51	0.48	-0.14	-0.24	-0.1	-0.48	-0.65	0.87	1	
AL-Org	0.49	0.73	0.79	0.7	0.65	0.39	0.37	0.68	0.77	-0.02	-0.0	0.02	-0.04	0.07	-0.17	-0.05	-0.22	-0.06	-0.06	-0.23	-0.4	1
S-Org	0.86	0.53	0.58	0.52	0.48	0.49	0.39	0.58	0.59	-0.1	-0.0	0.01	-0.06	-0.08	-0.32	-0.16	-0.31	-0.13	-0.01	-0.23	-0.5	0.58

NB: S – sediments; AL – Algae mats; Org – organic matter; n = 48, $p<0.01$

Both algae and sediment from Bodo creek accumulate metals in similar sequence, this order is in agreement with finding of [21] who showed that Fe and most other trace elements have a common source, which explains similar trends of metal accumulation in algae and sediment.

Correlation

A Pearson product-moment correlation coefficient was computed to assess the co-variation and relationships of metals among themselves or within the three major compartments of Bodo creek. Correlation matrix presented in Table 5 showed that positive correlations exist for same metals in algae and sediment respectively while negative insignificant correlations exist in water. Positive significant correlation existed between Mn and Fe and with most of the metals except Cd in all the matrices. Most metals were found to co-precipitate with or adsorbed on to Fe and Mn geochemical phases in sediments. However, Fe has higher affinity with most trace elements. This implies that these metals often sorbed to iron and manganese complexes. The metals in algae increase with decrease in pH. Except Zn &Cd, the metals in algae were significantly positive with each other. Also organic matter contents are important as controlling factors in the abundance of trace metals because of significant positive correlate with most metals in sediments. Cobalt and Nickel had the highest significant value for sediment and algal mat (0.98) which indicate that they were from the same source and occur together.

CONCLUSION

The distribution of trace metals in water, sediment and algal mat in Bodo creek indicates the health quality of the wetland systems of River Niger and provide insight on the biodegradation role of algae which is important for environmental management programs in the region. The physicochemical characteristics show that the trace metals accumulate more in stations with fine granulometric fractions, lower pH values and higher organic matter. Despite affinity of various algal species for binding to metal ions may differ, algae enhance the removal of metals and furnish O_2 to heterotrophic aerobic bacteria to mineralize organic pollutants [8]. The use of algae should be an option to consider in the cleanup of oil polluted Niger Delta region of Nigeria. Moreover, the use of biological processes for the treatment of metal enriched wastewaters has advantage over the use of physical and chemical treatments. It is more economical, environmental friendly and metal accumulation capacity of algal biomass is comparable with chemical sorbents.

Competing interests

The author declare no competing interest

ACKNOWLEDGEMENTS

The author acknowledged the assistance provided by Center for Marine Pollution and Seafood Safety, University of Port Harcourt

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